



# Use of activated carbon obtained from waste vine shoots in nickel adsorption in simulated stomach medium

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Received: 7 July 2021 / Revised: 1 September 2021 / Accepted: 12 September 2021  
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## Abstract

In this study, it is aimed to remove nickel from the simulated body fluid by adsorption technique in order to reduce its harmful effects on the human body. Activated carbon was used for the adsorption of Ni(II) pollutants that may occur in the simulated stomach medium. Activated carbon gave a very porous structure with different sizes of pores by presenting a morphology suitable for the adsorption process. The results show the efficiency of activated carbon with interesting surface area values ( $1689 \text{ m}^2 \text{ g}^{-1}$ ) and total pore volume ( $0.842 \text{ cm}^3 \text{ g}^{-1}$ ). The most suitable adsorption parameters for nickel ions in the stomach environment simulated in a batch system (pH, time, mixing speed, amount of adsorbent, and the effect of other ions, etc.) were investigated. The initial nickel ion concentration was  $10 \text{ mg L}^{-1}$  and the adsorbent amount was 0.3 g, and it was determined that the maximum retention efficiency of nickel ions in the pH range 3.5–5.5 was 92%. The activated carbon material was also highly effective, with a maximum of 91.8% removal at  $10 \text{ mg L}^{-1}$  of Ni(II) solutions. Finally, the prepared material has basic properties that make it an effective adsorbent in purifying the pollutants that occur in the simulated stomach medium and we recommend that it can be used to clean the stomach environment in nickel poisoning in emergency interventions.

**Keyword** Waste vine shoots · Activated carbon · Simulated stomach · Nickel · Adsorption

## Highlights

- An activated carbon material was prepared from vine shoot wastes.
- Activated carbon presented a morphology with favorable characteristics for the adsorption.
- Adsorption capacity was  $7.67 \text{ mg g}^{-1}$  for Ni(II).
- Activated carbon has essential characteristics to treat simulated stomach medium with emerging contaminants.

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## 1 Introduction

Nickel, which is one of the most common contaminants in water and agricultural areas, is easily transferred to various plants and poses a significant threat to human life [13, 18]. Nickel is shaped in nature due to human activities in addition to its natural diffusions; It is emitted into the atmosphere through the combustion of fuels, mining and refining

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processes, and the ashing of urban waste. Although nickel has no known biological function other than its presence in the urease enzyme, it has a moderate toxicity. The organic form of nickel is more toxic than its inorganic form. Accumulation of nickel is observed in tissues such as the lungs, intestines, and skin with the intake of high doses of soluble nickel salts or accidental consumption of nickel-contaminated water and nutrients [13]. In addition to irritating the skin, it has toxic and carcinogenic effects on the cardiovascular system [17]. It has toxic properties for some plant species in a certain overdose ( $0.18\text{--}5\text{ mg L}^{-1}$ ) [14]. Foods are recommended to contain less than  $150\text{ }\mu\text{g}$  of nickel per day [22].

The adsorption technique is a method used for years in the removal of toxic substances from the organism to reduce the harmful effects of toxic substances entering the human body for any reason [10]. Activated carbon is frequently used in the removal and destruction of hazardous components in liquid and gas phase [33]. In oral poisoning, activated carbon is the most common application for removing toxin from the body [1]. Activated carbon can adsorb toxic substances 10 times its own volume due to its porous structure. Since activated carbon is a substance that is not absorbed in the intestine, it also adsorbs the toxic substance and turns it into a non-absorbable state. However, the weak adsorption affinity of heavy metals to activated carbon used in the stomach environment at low pH is undesirable. This situation highlights the use of chelate as an alternative in heavy metal poisoning. The fact that chelating agents are expensive and the occurrence of undesirable effects make it important to use activated carbon types, which adsorb at low pH and are more inert than chelating agents, in this field.

Studies have shown that 69.1% of the toxin can be bound when activated carbon is applied in the first half hour after the ingestion of toxic substances, and 34.4% when given in the first hour. Another important feature of activated carbon is that it absorbs and binds some of the toxins that have been absorbed and mixed into the circulation by diffusion to the intestinal lumen and excreted. Thus, it almost functions as an intestinal dialysis [16, 25]. Rey-Mafull et al. [28] using a simulated stomach medium conducted a comparative adsorption study of acetaminophen on commercial activated carbon samples (Norit E Supra USP, Norit B Test EUR, ML) obtained from different sources. Comparison of three activated carbons with different activities showed that the microporous structure and surface chemistry play a critical role in defining their adsorption capacity. In a similar study in the literature [27], it was observed that 84% of cadmium ions were adsorbed by Shiitake mushroom, a functional food of  $65.12\text{ mg}$  simulated stomach medium with a pH of 6.0, and it was shown that the Shiitake mushroom was particularly effective in removing cadmium ions at low concentrations.

In this study, it is aimed to remove nickel from the body fluid by means of a solid phase extraction (adsorption) technique in order to reduce the harmful effects on the human health. A new activated carbon obtained from the waste vine shoots was used as the adsorbent (ACVS). In the batch system, the most suitable adsorption parameters (pH, time, mixing speed, amount of adsorbent, and the effect of other components, etc.) for nickel ions in the simulated stomach medium (SSM) were investigated.

## 2 Materials and methods

### 2.1 Equipment and materials

Metal determinations in the study were performed with Analytik Jena ContrAA 300 (GLE, Berlin, Germany) Model HR-CS FAAS. Instrumental parameters are set to the values given in the device catalog; In order to obtain the highest analyte signal, flame composition and flame head height were investigated. In this study, HANNA brand HI 2211 digital pH meter was used for pH measurements.

### 2.2 Preparation of simulated stomach medium

The composition given in Table 1, recommended by NIOSH (National Institute for Occupational Safety and Health), was prepared. It has been used as a simulated stomach medium (SSM). pH adjustments in the related experiments were made using dilute HCl and NaOH solutions in the presence of the mentioned pH meter.

### 2.3 Production and characterization of activated carbon

In the study, activated carbon obtained by chemical activation of dried and powdered waste vine shoots with  $\text{ZnCl}_2$  was used. Activated carbon was prepared by pyrolysis of samples activated by zinc chloride at a weight ratio of  $40\text{ g}/30\text{ g}$  (waste vine shoots/ $\text{ZnCl}_2$ ) at  $700\text{ }^\circ\text{C}$  [11].

It was found that the obtained activated carbon has  $1689\text{ m}^2\text{ g}^{-1}$  BET surface area and  $0.842\text{ cm}^3\text{ g}^{-1}$  total pore volume, and also contained 89.65% carbon and had a pH<sub>zpc</sub> value of 4.8. In order to determine the adsorption property of activated carbon on the surface, the iodine number was determined as  $1276\text{ mg g}^{-1}$  [11].

Carboxylic groups, lactans, and phenolic groups are “acidic” surface oxides. Boehm identified these acidic groups by neutralizing them with different bases. Acidic groups were determined as 0.0484, 0.1082, 0.095, and  $0.02367\text{ meq g}^{-1}$  by the Boehm titration method [8], respectively. It has been determined by us that it has significant acidic surface functional groups by Boehm titration

**Table 1** Comprehensive simulated stomach medium composition recommended by NIOSH [31]

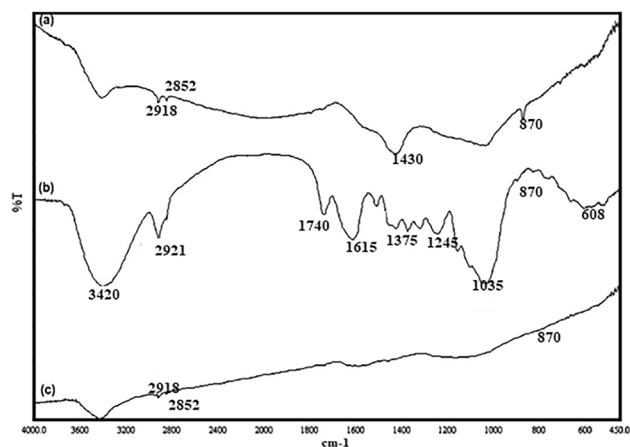
*Component	Amount (g L <sup>-1</sup> )
<b>Electrolytes and ionic components</b>	
Calcium chloride dihydrate (CaCl <sub>2</sub> ·2H <sub>2</sub> O)	0.2646
Magnesium chloride hexahydrate (MgCl <sub>2</sub> ·6H <sub>2</sub> O)	0.1525
Potassium chloride (KCl)	0.8647
Sodium chloride (NaCl)	2.8559
0.04 M hydro chloric acid (HCl)	1.4263
Sodium bromide (NaBr)	0.0008
Copper (II) chloride dihydrate (CuCl <sub>2</sub> ·2H <sub>2</sub> O)	0.0003
Sodium fluoride (NaF)	0.0009
Phosphorus pentachloride (PCl <sub>5</sub> )	0.4707
<b>Organic acids and carbohydrates</b>	
D (+)-Fructose (C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> )	0.1380
D (+)-Glucose (C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> )	0.3500
D (+)-Sodium salt of glucuronic acid, monohydrate (C <sub>6</sub> H <sub>9</sub> NaO <sub>7</sub> ·H <sub>2</sub> O)	0.0241
Sialic acid (C <sub>11</sub> H <sub>19</sub> NO <sub>9</sub> )	0.0731
Amino acid tablet	0.2672
<b>Nitrogenous compounds</b>	
1 M ammonium hydroxide (NH <sub>4</sub> OH)	0.1996
Urea (CH <sub>4</sub> N <sub>2</sub> O)	0.0840
Uric acid (C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O <sub>3</sub> )	0.0080
Vitamin tablet	0.9502
Pepsin	3.2000

\*All chemicals used were of analytical purity from Merck Company, Darmstadt, Germany, and Fluka, Switzerland

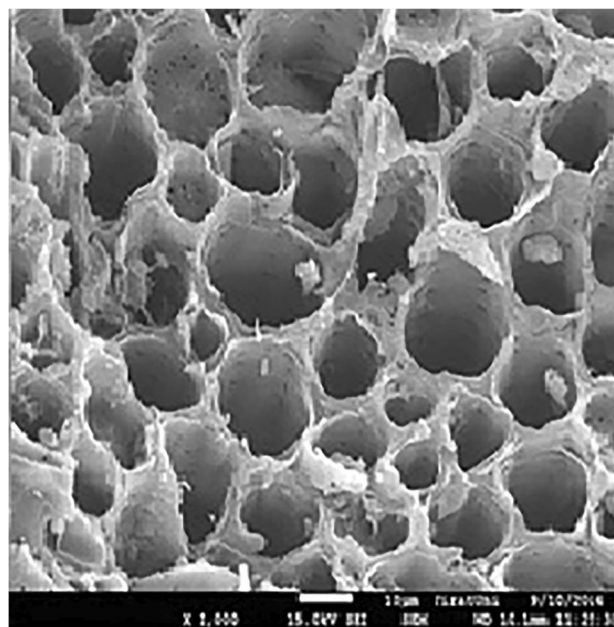
on activated carbon. Especially the presence of carboxylic groups is compatible with the values obtained by Boehm titration.

The absorbance (or transmittance) values of the functional groups were determined in order to know the functional groups and their changes in the original and treated waste vine shoot samples. For this purpose, FT-IR spectrum of activated carbon is given in Fig. 1, elemental analysis results are given in Table 2, and SEM image in 700 °C heat treatment is given in Fig. 2.

In the FT-IR spectrum of the activated carbon given in Fig. 1, (a) is the activated carbon obtained at 700 °C, (b) the raw vine shoots, and (c) the activated carbon activated with ZnCl<sub>2</sub>, and peaks are seen at 3400 cm<sup>-1</sup> in all three samples. It shows the presence of alcohol, phenol, and carboxylic groups as indicators. Peaks between 2850 and 2920 cm<sup>-1</sup> show C-H structure, 1740 cm<sup>-1</sup> C=O structure, 1614 cm<sup>-1</sup> C=C structure, and 1510 cm<sup>-1</sup> C-C structure. Peaks at 600–870 cm<sup>-1</sup> show that the structure has an aromatic ring structure in two bands. According to the elemental analysis results given in Table 2, it can be considered high quality when compared with the activated carbon values in the literature [5, 6].

**Fig. 1** FT-IR spectrum of activated carbon used in experiments ((a) activated carbon obtained at 700 °C; (b) raw vine shoots; (c) activated carbon activated with ZnCl<sub>2</sub>) [11]**Table 2** Elemental analysis results of activated carbon used in experiments [11]

C: 89.65	N: 1.58	H: 0.71	S: 0.062	O: 8.00
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**Fig. 2** SEM image of the activated carbon obtained at 700 °C used in the experiments [11]

The channels, voids, and large outer surface cracks in the SEM image of the activated carbon in Fig. 2 have shown high adsorption properties with sufficient pore size, large surface area, and a highly porous structure [12].

## 2.4 Adsorption process with activated carbon

The adsorption studies made with the activated carbon obtained are given in Fig. 3.

In the end, the residual concentration of Ni(II) was determined by Analytik Jena ContrAA 300 HR-CS FAAS, and the responses pollutant to removal (Ni(II) adsorption %) and adsorption capacity were determined by Eqs. 1 and 2, respectively.

$$\text{Ni(II) adsorption \%} = (C_0 - C_s) \times \frac{100}{C_0} \quad (1)$$

$$q = \frac{(C_0 - C_s) \times V}{m} \quad (2)$$

where  $m$  is the mass of ACVS (g),  $V$  is the solution volume (L), and  $C_0$  and  $C_s$  are the initial and equilibrium concentrations of the adsorbate solution ( $\text{mg L}^{-1}$ ).

Reduction and adsorption experiments were carried out in two parallel examples. When the results deviated at most 3% from each other, calculations were made by taking the average of two parallel experiments. A third experiment was performed in cases with few, but more deviations, and the average of two close experiments was taken into account.

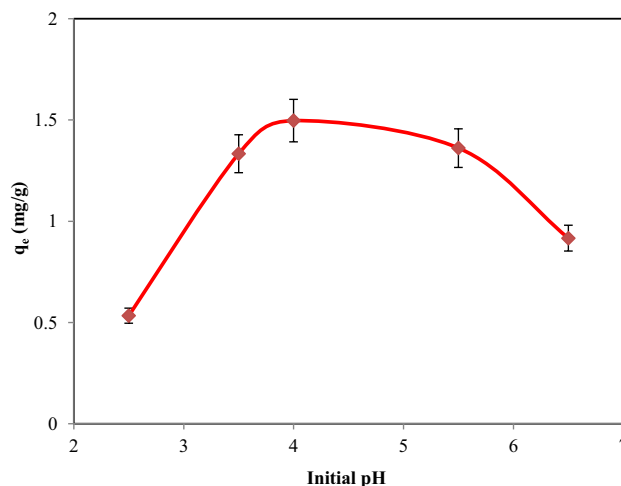
## 3 Results and discussion

### 3.1 Effect of pH on the adsorption of Ni(II)

The parameters affecting the adsorption of Ni(II) ions are given below. In the batch system in which ACVS was used as

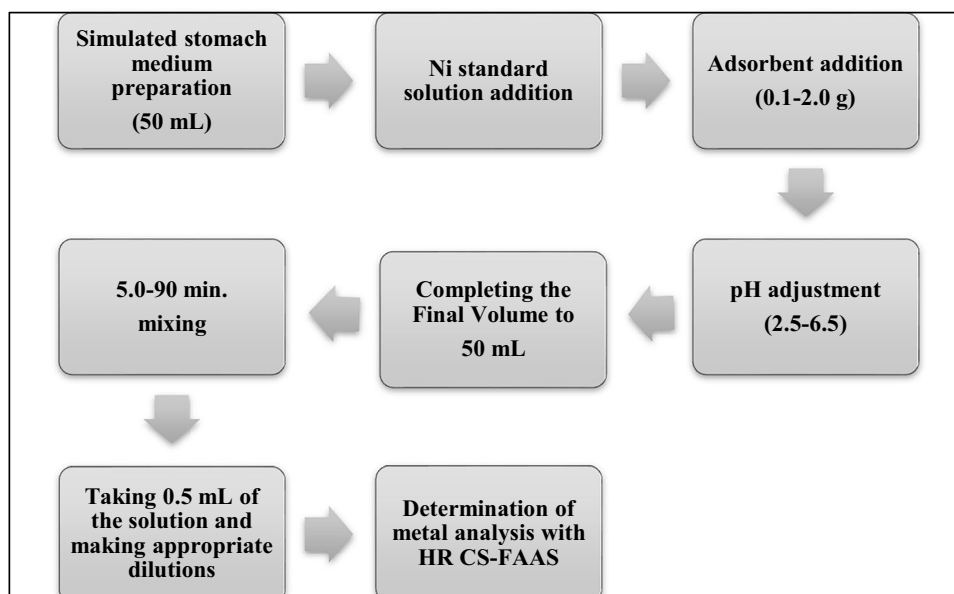
an adsorbent, the initial nickel ion concentration was  $10 \text{ mg L}^{-1}$  and the adsorbent amount was 0.30 g. In order to determine the effect of pH on the adsorption of Ni(II) ions, it has been studied in the range of pH 2.5–6.5. According to the first results, the graph showing the adsorption capacity ( $q_e$ ) change at different pH is given in Fig. 4.

When we examined the effect of pH on the adsorption of Ni(II) ions, the pH of the adsorption medium is one of the most important parameters affecting the adsorption of heavy metal ions on the active carbon surface. It has been observed that between pH 3.5 and 5.5, the adsorption capacity is high and below pH 3.5 and above pH 5.5, the adsorption capacity



**Fig. 4** The effect of pH on the adsorption of Ni(II) ions (sample volume: 50 mL,  $C_0$ :  $10 \text{ mg L}^{-1}$ , mixing speed: 200 rpm, contact time: 90 min, adsorbent dosage: 0.3 g ACVS)

**Fig. 3** Adsorption process with activated carbon



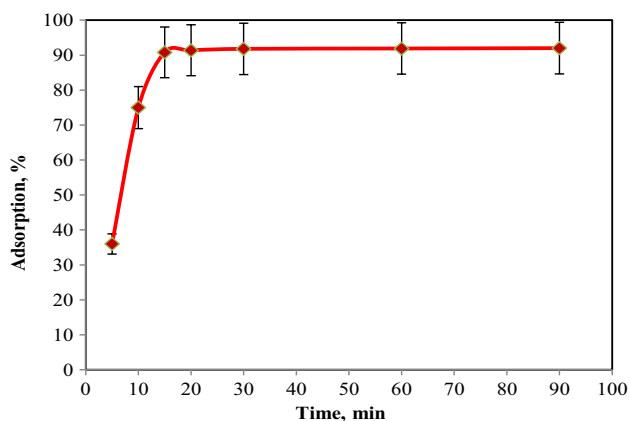
decreases. In our next study, the studies were continued at pH 4.0, taking into account the pH of the stomach medium.

While the amount of Ni(II) adsorbed at high pH is low, it first increases a little with the decrease in pH and then decreases again. It can be said that this situation is caused by the change in the pH and surface loads of activated carbon and the change in the removal of Ni(II) amounts depending on the pH. It is stated in previous studies that the net zero proton load (pHzpc) point for activated carbon is 4.8. This means that above pH value the surface is partially negatively charged and partially positively charged below it. Therefore, around this pH value, the amounts of negative and positive charges on the surface are close to each other. As the pH decreases, the surface becomes positively charged and becomes incompetent for adsorbing positively charged Ni(II) species. Therefore, it is expected that the adsorption capacity will decrease due to the decrease in the adsorption of Ni(II) first with increasing acidity. Finally, it can be thought that the lower initial pH than the final pH of the mixture is due to the acidic materials in activated carbon structure [3, 7].

### 3.2 Effect of contact time on the adsorption of Ni(II)

When we examined the effect of contact time on the adsorption of Ni(II) ions, it was studied between 5 and 90 min at 200 rpm mixing speed at an initial nickel ion concentration of  $10 \text{ mg L}^{-1}$  in 50 mL sample volume to determine the appropriate contact time. According to the results, the graph showing the change of adsorption efficiency (%) of Ni(II) ions at different contact times is given in Fig. 5. It was seen that the highest adsorption efficiency was 20 min and it was continued as 20 min in our next study.

In a similar study [32], in the method developed for the potential use of alginate gel beads in the treatment of acute lead poisoning, the adsorption kinetics of 50 to 200  $\text{mg L}^{-1}$

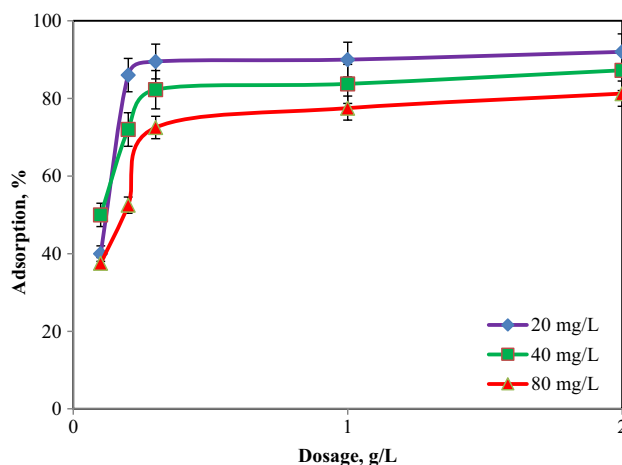


**Fig. 5** The effect of contact time on the adsorption efficiency of Ni(II) ions (sample volume: 50 mL, pH: 4.0,  $C_0$ :  $10 \text{ mg L}^{-1}$ , mixing speed: 200 rpm, adsorbent dosage: 0.3 g ACVS)

lead concentrations at pH: 2.5 at  $37^\circ\text{C}$  in a simulated stomach medium were investigated. It was observed that the swelling rate of dry beads increased significantly over time. It was observed that adsorption of Pb (II) by dry beads increased with increasing time and initial lead concentration in the simulated stomach medium. Adsorption kinetics of Pb (II) by hydrated alginate particles, Pb (II), were rapidly absorbed during the first 15 min for all concentrations.

### 3.3 Effect of adsorbent dosage on the adsorption of Ni(II)

In order to determine the effect of the adsorbent amount on the adsorption of Ni(II) ions, experiments were carried out in 50 mL sample volume, 20–40–80  $\text{mg L}^{-1}$  initial nickel ion concentration, and 0.1–2.0 g adsorbent amount. According to the results, the graph showing the change of adsorption efficiency (%) of Ni(II) ions in different adsorbent amounts and different nickel ion concentrations is given in Fig. 6. The best adsorption efficiency was achieved with an adsorbent amount of 0.3 g. In the next studies, it was continued by using 0.3 g activated carbon. In a similar study in the literature, Panthee and Lohani [26] used active carbon in capsule, powder, and suspended form for the adsorption of paracetamol. The adsorption capacity of paracetamol in simulated stomach medium (pH 3.4) and artificial intestinal fluid (pH 7.2) was determined. Activated carbon and paracetamol were mixed at both pH and the paracetamol content was determined by a UV spectrophotometer. The highest adsorption capacity was determined using the Langmuir adsorption isotherm. It has been determined that the effect of pH on the adsorption capacity is not significant. Under artificial environment conditions, three formulations of activated carbon adsorbed sufficient amount of paracetamol. The data showed



**Fig. 6** The effect of the amount of adsorbent on the adsorption efficiency of Ni(II) ions (sample volume: 50 mL, pH: 4.0, mixing speed: 200 rpm, contact time: 20 min)



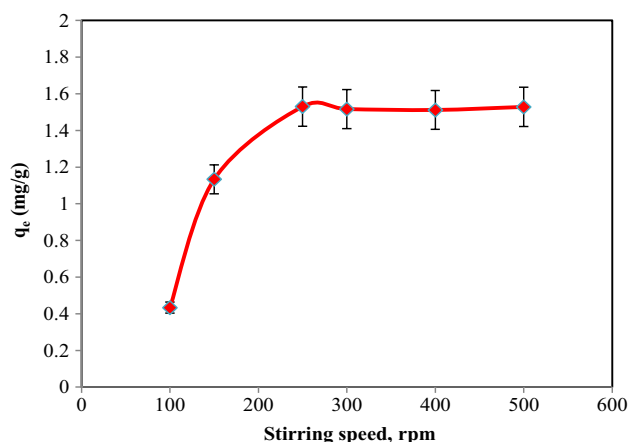
that 1 g per kg of activated carbon given shortly after paracetamol poisoning would suffice.

### 3.4 Effect of mixing speed on the adsorption of Ni(II)

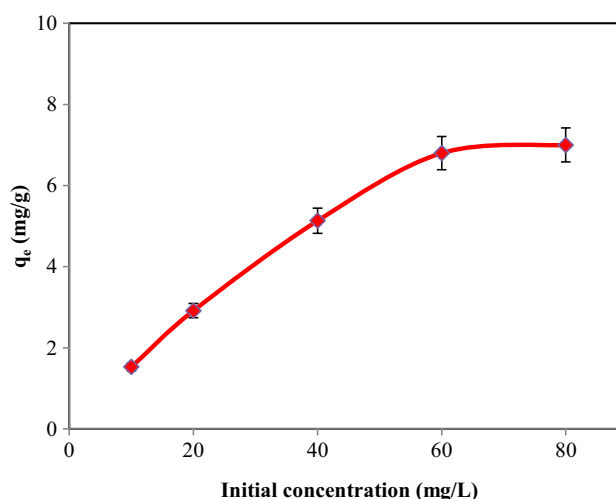
In our study, where we examined the effect of mixing speed on the adsorption of Ni(II) ions, in order to determine the appropriate mixing speed, 50 mL sample volume, 10 mg L<sup>-1</sup> initial nickel ion concentration, and 100–500 rpm stirring speed range were studied. According to the results, the graph showing the change of adsorption capacity ( $q_e$ ) of Ni(II) ions at different mixing speeds is given in Fig. 7. In a study where we examined the effect of mixing speed on the adsorption of Ni(II) ions, the highest adsorption capacity was reached at 250 rpm in the study we conducted at 100–500 rpm. It has been observed that the adsorption capacity up to 500 rpm is high. In our next work, it was continued at 250 rpm.

### 3.5 Effect of initial Ni(II) concentration on the adsorption of Ni(II)

In the study investigating the effect of initial nickel concentration on the adsorption capacity, a sample volume of 50 mL was studied between the initial nickel concentration of 10 and 80 mg L<sup>-1</sup>. According to the results, the adsorption capacity ( $q_e$ ) change against the concentration of Ni(II) ions is given in Fig. 8 and the adsorption efficiency % is given in Table 3. It was observed that as the initial nickel ion concentration increased, the adsorption capacity increased and stabilized after 60 mg L<sup>-1</sup> (Fig. 8). It reached saturation in a shorter time due to the increase in concentration. It was observed that as the initial nickel ion



**Fig. 7** The effect of mixing speed on the adsorption of Ni(II) ions (sample volume: 50 mL,  $C_0$ : 10 mg L<sup>-1</sup>, pH: 4.0, contact time: 20 min, adsorbent dosage: 0.3 g ACVS)



**Fig. 8** The effect of Ni(II) ion concentration on the adsorption capacity (sample volume: 50 mL, pH: 4.0, stirring speed: 250 rpm, contact time: 15 min, adsorbent dosage: 0.3 g ACVS)

concentration increased, the equilibrium values increased and the yield values decreased (Table 3).

Rey-Mafull et al. [28] using a simulated stomach medium conducted a comparative adsorption study of acetaminophen on commercial activated carbon samples (Norit E Supra USP, Norit B Test EUR, ML) obtained from different sources. Acetaminophen with  $C_0 = 2500$  mg L<sup>-1</sup> was mixed in an artificial stomach environment at pH 1.2 for 4 h in a 37 °C water bath and contacted with activated carbon. Results were determined using UV visible and evaluated using adsorption isotherms. Comparison of three activated carbons with different activities showed that the microporous structure and surface chemistry play a critical role in defining their adsorption capacity. In a similar study in the literature [27], it was observed that 84% of cadmium ions were adsorbed by Shiitake mushroom, a functional food of 65.12 mg simulated stomach medium with a pH of 6.0, and it was shown that the Shiitake mushroom was particularly effective in removing cadmium ions at low concentrations.

**Table 3** The effects of initial Ni(II) ion concentration on % adsorption efficiency

$C_0$ (mg L <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	Adsorption, %
10	1.53	91.8
20	2.92	87.5
40	5.13	77.0
60	6.8	68.0
80	7.0	52.5

**Table 4** The effect of components in the simulated stomach medium on the adsorption efficiency of Ni(II) ions

Component	Ni(II) adsorption, %
KCl (0.5 g)	90 ± 2
PCl <sub>5</sub> (0.5 g)	91 ± 2
NaCl (1.5 g)	92 ± 1
MgCl <sub>2</sub> ·6H <sub>2</sub> O (0.3 g)	89 ± 2
CH <sub>4</sub> (N <sub>2</sub> O) (0.2 g)	90 ± 2
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (0.5 g)	89 ± 3

### 3.6 Effect of other components on the adsorption of Ni(II)

In the study investigating the effect of other components on the adsorption of Ni(II) ions in a simulated stomach medium, an initial Ni(II) concentration of 10 mg L<sup>-1</sup> was examined in a sample volume of 50 mL. The adsorption efficiency of Ni(II) ions was determined by adding the excess components (KCl (0.5 g), PCl<sub>5</sub> (0.5 g), NaCl (1.5 g), MgCl<sub>2</sub>·6H<sub>2</sub>O (0.3 g), CH<sub>4</sub>(N<sub>2</sub>O) (0.2 g), C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> (0.5 g)) in the simulated stomach medium separately to these samples. The results obtained are given in Table 4.

In the study investigating the effect of other components in the simulated stomach medium on the adsorption of Ni(II) ions, it was observed that the excess of the components in the simulated stomach medium did not have a significant effect on the adsorption efficiency of Ni(II) ions (Table 4). In a similar study in the literature [19], the use of a new activated carbon obtained from date seeds in paracetamol poisoning by using artificial gastric and intestinal fluids that do not contain enzymes was investigated. In the study, liquids prepared with paracetamol at a ratio of 15:1 w/w were contacted with the adsorbent for 60 min and showed that the obtained activated carbon could be used in paracetamol poisoning.

### 3.7 Adsorption isotherm

The study of adsorption isotherms allows defining the molecular distribution of adsorbate in solution at equilibrium and therefore to obtain details such as the mechanism of absorption and the affinity of the nickel towards the adsorbent surface. To do this, we analyzed the adsorption results by two isothermal models: Langmuir and Freundlich.

The capacity of the adsorbent was investigated in order to evaluate to what extent the activated carbon obtained from the waste vine shoots of Ni(II) ions can be adsorbed. According to the Langmuir equation, taking into account the analyte concentration in the solution ( $C_e$ ) and the amount of

analyte adsorbed on the unit adsorbent ( $q_e$ ), the  $C_e/q_e$  versus  $C_e$  values are plotted (Fig. 9) (Eq. 3) [21].

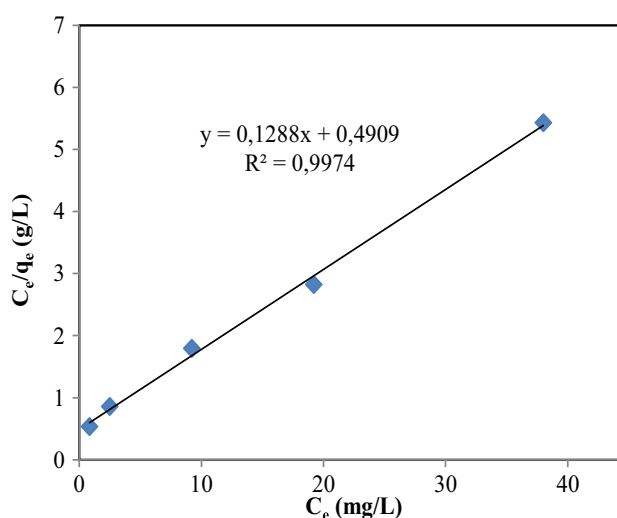
$$\frac{C_e}{(x/m)} = \frac{1}{q_{\max}K} + \frac{C_e}{q_{\max}} \quad (3)$$

The adsorption, according to the Freundlich model, is characterized by the following properties: The adsorption systems are heterogeneous, the energy of the reaction varies according to the quantity adsorbed, the adsorption sites are distributed exponentially as a function of the heat of adsorption, and the existence of an interaction between the adsorbed molecules. The conformity of the Freundlich isotherm hypotheses with the experimental data could be verified using the following mathematical equation (Eq. 4):

$$\ln(x/m) = \ln K_f + \frac{1}{n_f} \ln C_e \quad (4)$$

The correlation coefficient ( $R^2$ ) in the studies for the adsorption of Ni(II) was determined as 0.9974. From the  $R^2$  value of the obtained line, the compatibility of the adsorption behavior with the Langmuir model was evaluated. The data obtained reveal that the adsorption occurs as a single layer on the surface [9]. In addition, the maximum adsorption capacity ( $q_{\max}$ ) and adsorption energy constant ( $K$ ) were calculated from the slope of this line ( $1/q_{\max}$ ) and the cutoff point (Fig. 9). The  $q_{\max}$  and  $K$  values for Ni(II) were determined as 7.67 mg g<sup>-1</sup> and 0.262 L mg<sup>-1</sup>, respectively.

The experimental results of the adsorption isotherms of nickel on ACVS are modeled by different equations of Langmuir and Freundlich. Results found shows that the Langmuir isotherm better describes the adsorption isotherm of the nickel on the ACVS adsorbent with a determination coefficient of the order of 0.9974 and an equivalent theoretical

**Fig. 9** Langmuir adsorption isotherm

adsorption quantity to the experimental adsorption amount. Adsorption is thought to be low for values of  $n_F$  less than 1. Adsorption is relatively challenging when  $n_F$  values are in the range of 1 to 2. The computed values of the Freundlich equation's parameter  $n_F$  demonstrate that the adsorption onto the ACVS adsorbent surface is moderately difficult for nickel.

### 3.8 Adsorption kinetic

The adsorption kinetics consists of determining the adsorption reaction time between adsorbent-adsorbate. It also makes it possible to determine the contact time influence between the adsorbate and the adsorbent. Adsorption kinetics are characterized by the rate of transfer of a solute in solution to the surface of an adsorbent. Fitting the experimental data with kinetic models can predict the mechanisms that control the adsorption process. There are many models to describe adsorption over time, but the majority of these are based on pseudo-first-order and pseudo-second-order.

The pseudo-first-order model assumes that the adsorption rate at time  $t$  is proportional to the difference between the amount adsorbed at equilibrium  $q_e$  and the amount  $q_t$  adsorbed at that time and that the adsorption is reversible (Eq. 5).

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \quad (5)$$

As depicted in the adsorption kinetics plot (Fig. 10), the adsorption increases strikingly and reaches its equilibrium at 7.6 mg/g within the first 20 min at the initial Ni(II) concentration of 10 mg/L. To determine the kinetics, the plot

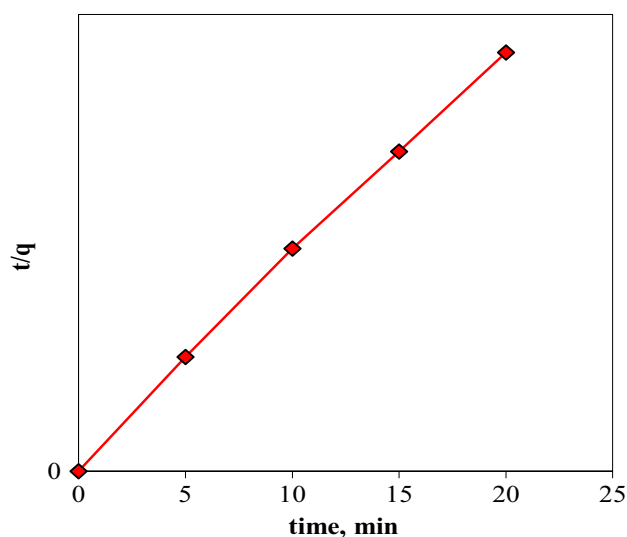


Fig. 10 Ni(II) adsorption kinetics

was fitted with a pseudo-second-order kinetic model shown in Eq. (6) [15].

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \quad (6)$$

Here,  $q_e$  and  $q_t$  are the adsorbed amounts at equilibrium and at time  $t$  (min) and  $k_2$  is a rate constant. The coefficient of determination ( $R^2$ ) of the curve fit was found to be 0.9999, signifying that the data are very well fit with the chosen kinetic model. The calculated  $q_e$  is 7.36 mg/g, comparable to the experimental value. The rate constant ( $k_2$ ) is found to be  $1.08 \times 10^{-3}$  g/mg min, which is comparable to those reported in the literature. The fast equilibration and adsorption can be attributed to the hierarchical microporous-mesoporous structure in the material. The interconnected macropores from the waste vine shoot arrangement of the fibers will facilitate diffusion of solvent and adsorbate, while the micropores generated during the pyrolysis in the presence of pore activating agent are responsible for the adsorption and confinement of Ni(II) [20, 23].

The experimental results of linear adsorption kinetics regressions were examined. The pseudo-second-order model may be better suited to describe the adsorption kinetics mechanism of nickel on the ACVS with the same coefficient of determination  $R^2 = 0.9999$ .

Therefore, it can be concluded that the pseudo-second-order kinetic model can more accurately describe the kinetic effects of Ni(II) in activated carbon adsorption solution. This can be possibly explained that the Ni(II) adsorption process of activated carbon to water was mainly controlled by the chemisorption mechanism rather than by material transport step [5].

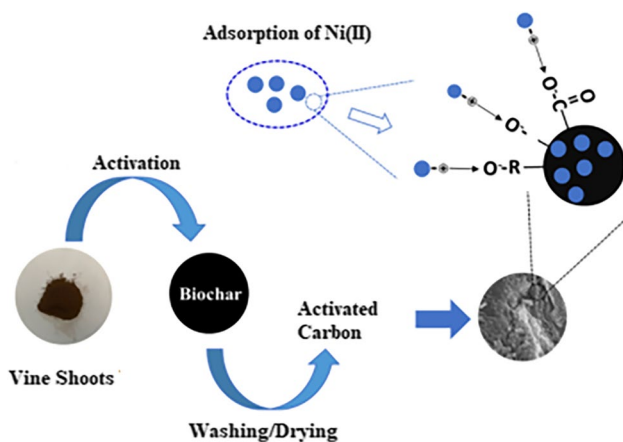
Some adsorbents used in the adsorption of nickel ion in the literature and the resulting adsorption capacity and efficiency are given in Table 5. It has been determined that the activated carbon obtained from waste vine shoots has a capacity comparable to the literature in the removal of nickel ions.

The preparation protocols and the performances of materials, in terms of adsorption capacity and adsorption rate towards Ni(II), are compared with other previously reported porous materials (carbon-based adsorbents). The materials were selected based on their adsorption capacity, which is in the top ranks for each group of materials. The adsorption capacity of the present carbon sorbent is among the best values reported so far. Although, it is not as high as those of the waste-derived nitrogen-doped hierarchical porous carbon, the hydrochar derived from wastes. Furthermore, its equilibration time is also comparable or even faster than of prior adsorbents. Concerning the preparation protocols, the present work offers less and greener steps. Neither chemicals (i.e., KOH, HCl,  $H_2SO_4$ ), toxic solvents (i.e., acetone, DMF) nor tedious filtration steps are needed. In comparison to other porous adsorbents (i.e., MOFs, silica, and carbon nanomaterials),



**Table 5** Parameters obtained from studies on the adsorption of nickel ion

Adsorbent	Adsorption medium	pH	Adsorption capacity (mg g <sup>-1</sup> )	Adsorption, %	Contact time	References
Granular activated carbon	Aqueous solution	5.0	0.130	55.0	75 min	[23]
Activated carbon obtained from apricot kernel	Aqueous solution	4.0	26.96	97.59	90 min	[20]
Activated carbon obtained from grape marc	Aqueous solution	4.0	-	92.3	60 min	[24]
Activated carbon from Himalayan pine	Aqueous solution	4.0–4.5	31.4	95.6	180 min	[29]
Activated carbon obtained from vine shoots	Simulated stomach medium	4.0	7.67	> 90	20 min	This work

**Fig. 11** Adsorption mechanism

carbon materials offer cheaper starting materials than MOFs and porous silica, and better chemical and thermal stability than MOFs, as well as lower cost and less complicated production than other carbon nanomaterials [2, 12, 30].

### 3.9 Adsorption mechanism

The adsorption mechanism of Ni(II) on the material is proposed in Fig. 11. As evidenced by FT-IR, the sp<sup>2</sup> carbon is the dominant carbon functionality found on the composite surface. Additionally, the SEM result also confirms the presence of graphitic carbons [2]. As Ni(II) has +2 charged ion in its structure, it could offer  $\pi$  electrons to interact with the graphitic carbons via  $\pi$ - $\pi$  interactions. Hence, it is believed that these  $\pi$ - $\pi$  interactions might play a key role in Ni(II) adsorption. Besides  $\pi$ - $\pi$  interactions, hydrogen bonding between oxygen-containing functionalities and the hydroxyl group of Ni(II) as well as hydrophobic interactions could also partly contribute to this adsorption. As the molecular size of Ni(II) matches well the generated pore size, the adsorption of Ni(II) inside these pores is expected. This can be confirmed by the aforementioned result where the adsorption capacity of Ni(II) increased with the pore surface area (BET). Therefore, the high adsorption capacity

of the activated carbon towards Ni(II) might be attributed not only to the proper adsorbate/adsorbent interactions but also to the high porosity and the large carbon surfaces [34].

## 4 Conclusion

In this study, it is aimed to remove nickel from food and water or other reasons from the organism by a solid phase extraction (adsorption) technique in order to reduce its harmful effects on the human body. The most suitable adsorption parameters (pH, contact time, mixing speed, adsorbent amount, and the effect of other components) were investigated for nickel ions from the simulated stomach medium in the batch system using a new activated carbon obtained from the waste vine shoots as the adsorbent. Waste vine shoot waste, a waste generated in large quantities from grape waste, was transformed into an efficient activated carbon material, capable of treating effluents contaminated with Ni(II). The surface area of the obtained activated carbon was found to be 1689 m<sup>2</sup> g<sup>-1</sup>, and the average pore volume was found to be 0.842 cm<sup>3</sup> g<sup>-1</sup>. SEM images showed morphological characteristics favorable to the adsorption process. The adsorption for Ni(II) was favored under acidic conditions and with a dosage of 0.3 g. The maximum adsorption capacity was 7.67 mg g<sup>-1</sup> for Ni(II). Besides, a removal percentage of 92.4% for Ni(II) was presented. Finally, activated carbon can be considered an efficient adsorbent to treat simulated stomach medium with emerging contaminants. It was also possible to convert a solid waste with no added value and produced in large quantities into an adsorbent material with great potential to treat effluents with Ni(II), thus turning a problem into a low-cost environmental solution. Activated carbon, which is an economical and natural product, is applicable for nickel adsorption in emergency applications.

**Author contribution** Çiğdem Er Çalışkan: investigation, supervision, experimental studies. Harun Çiftçi: supervision, funding acquisition, conceptualization, methodology, validation. Tacettin Çiftçi: investigation, experimental studies. Ergin Kariptaş: methodology, project administration, funding acquisition. Hasan Arslanoğlu: formal analysis,

writing—original draft, writing—review and editing, visualization. Mehmet Erdem: adsorbent synthesis and characterization.

**Funding** This study was financially supported by the Scientific Research Projects Unit of Kırşehir Ahi Evran University (Project No: FEF.A3.17.008).

## Declarations

**Competing interests** The authors declare no competing interests.

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